Investigation and Site Restoration following a Major Accident Involving Hazard Classification 1.2 Ammunition

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Abstract

The results of the scientific studies into why an accident occurred at a Finnish ammunition depot are reported along with details of the position and type of the debris produced during the event. The Official Accident Investigation Board concluded that the most likely cause of the accident was auto-ignition of a propellant. After the accident, the rate of ammunition disposal was increased and a new regime for ammunition propellant testing was introduced in Finland.

Introduction

An accident which occurred just after 7pm on 19th July 1999, completely destroyed a magazine and resulted in ordnance and energetic materials being spread over a wide area. The net explosive content of the magazine was around 28000 kg. A guard, who had passed the magazine just five minutes before the incident began, initially heard a sound that was similar to that of a shotgun discharge. This sound continued every few seconds but after about one minute the rate increased and the sound changed to become more metallic. Statements given by people located three kilometres away and trials performed for the investigation board confirmed his report. The guard raised the alarm and within five minutes he had climbed a watchtower positioned some 300 m from the magazine. By this time, the explosions were larger and more regular. All the guard could see from the tower were large amounts of smoke in the area of the magazine. The large explosions which continued for around 90 minutes were followed by a period when a number of smaller single explosions were heard. The time between the explosions increased but some single events occurred several days after the initial event.

No personnel were injured by the accident but it took more than four days for helicopters and planes to extinguish the fire using water. An official accident investigation board concluded that the accident resulted from the auto-ignition of a propellant [1].

The investigation established that the unheated and unventilated storage facility contained several types of hazard classification 1.2 ammunition awaiting disposal. The energetic materials in

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14. ABSTRACT
The results of the scientific studies into why an accident occurred at a Finnish ammunition depot are reported along with details of the position and type of the debris produced during the event. The Official Accident Investigation Board concluded that the most likely cause of the accident was auto-ignition of a propellant. After the accident, the rate of ammunition disposal was increased and a new regime for ammunition propellant testing was introduced in Finland.

15. SUBJECT TERMS

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the 40 mm calibre rounds included high explosives (mainly TNT, with an explosive content of between 40 g and 70 g), fuzes containing detonators and boosters, an ignition propellant (approximately 1 g), double and single based propellants (typically weighing 275 g), many rounds contained a pyrotechnic tracer (each containing 10 g to 40 g of pyrotechnic). The packaging was either wood or fibreboard. The net explosive content of the magazine equated to several thousand kilograms. Four of the six main tracer compositions contained magnesium and strontium nitrate, one formulation contained strontium peroxide and another barium nitrate. The tracer priming compositions were either gunpowder or magnesium-barium peroxide formulations. Most of the ammunition was procured during the 1960s and 1980; some of the ammunition had been previously stored for an extended period under tarpaulins.

The magazine was of a lightweight construction with a timber clad frame and sheet metal roof, it was located in an open area on slightly raised ground. It did not have an electricity supply. For the preceding six weeks the ambient temperature in this area of Finland had been high with temperatures of 30 °C being recorded. Under similar conditions, the temperature inside a comparable facility was found to be as high as 60 ºC. During the restoration of the site, which took almost ten years, the position of each item of ordnance was accurately determined.

As a result of the accident a number of investigations were undertaken [2, 3] these included a statistical analysis on historical propellant stabiliser levels and a detailed study on the ageing of magnesium-strontium nitrate tracer compositions.

Mapping of the accident debris

The entire contents of the magazine were destroyed through burning, deflagration or detonation. A very minor portion of the material survived as complete rounds. The magazine itself was totally destroyed even the base which was concrete.

Debris was ejected over a wide area including two potentially very hazardous events. In one case, part of a projectile, which had detonated, went through the roof of a second magazine. The debris penetrated a package which included the cartridge case of a 120 mm munition. The propellant inside ignited but fortunately the fire extinguished before it could propagate to any other ammunition containers. In another case, a burning tracer penetrated the wall of a magazine. It stopped under a wooden pallet of ammunition containers. The tracer ignited the pallet and a 0.5 m length of the pallet was consumed before the fire self-extinguished.

The positions of more than twelve thousand items of ordnance were recorded during the operation to restore the site. A summary is presented in Table 1. Approximately 75% of the items were recovered from an area within 50 m of the magazine and more than 99% were found within 100 m distance. The majority of the 55 ordnance found more than 100 m from the magazine were tracers, but there were 23 other larger items; one fuze and one tracer were projected over 400 m.

The ammunition therefore behaved as described in the UN Orange Book [4] for 1.2 hazard classification and gave a projection hazard but not a mass explosion.

Statistical study on propellant stabiliser content

The objective of this statistical study [3] was to determine if there was a correlation between stabiliser content and the age or geometry of the single, double and triple based propellants. The original lot sizes of the propellants examined ranged from 10 000 kg to 30 000 kg. They were stored in one of four magazine types either light storage, dry storage, an earth-covered building or cave conditions but within lots the storage conditions were found to be diverse. The annual temperature and humidity ranges experienced during storage were wide but typically –50 °C to +60 °C and from 10% to 100% respectively. In general, accurate data were unavailable for individual samples or lots. The starting stabiliser levels for most of the individual lots were known and some materials had been mechanically blended to give new mixed propellant lots.

The different nitrocellulose propellant types were categorised into two groups, in the first group were all the single-based propellants and in the second were the double and triple-based ones. The historical data utilised for the study consisted of 7285 stabiliser measurements on 1688 different propellant lots and 72 different propellant types. As shown in Table 2, most of the data were on single based propellants with an average sample size of 158 determinations for each type of propellant and up to 40 results on a single lot of propellant. The stabiliser levels had been determined using High Performance Liquid Chromatography (HPLC), with the sample size for each single measurement being 100mg.

The stabiliser for the single-based propellants was diphenylamine, the double and triple-based propellants contained either methyl or ethyl centralite. Although akardite was the stabiliser in some lots there were insufficient samples for a statistical analysis on these propellant samples.

The data on individual propellant lots were classified into eight groups, generally 5 years in each group but rising to 10 and then 30 years for the final two groups respectively (Table 3). There were typically 3-10 observations in each group. For each propellant lot the arithmetic mean, standard deviation, kurtosis and skewness were determined [5, 6, 7].

On average, more than five times as many tests were performed on single based propellants compared to the combined double and triple based propellants; many of the single based propellants had stabiliser levels below 0.5 % and in one, the amount was less that 0.1 %. Based on limited data, propellants containing ethyl centralite were generally more stable than those containing the other stabilisers. Increasing the number of samples analysed raised the probability of finding a low level of stabiliser. No relationship was found between propellant grain size and stabiliser content. Other external factors were found to have a greater affect on the stabiliser

content than propellant age. The quality of manufacture also had a significant affect on the stabiliser level.

The ageing behaviour of magnesium-strontium nitrate pyrotechnic compositions

Fast burning magnesium-strontium nitrate pyrotechnic compositions are often used as tracers in direct fire ammunition. They are usually consolidated at high pressure into a metal tube and primed with a composition which is designed to resist the hight pressure regime experienced during gun launch. The tracer produces an essentially constant light output which allows the trajectory of ammunition to be observed during flight. This allows a correction to be applied to the aim of the weapon system.

All pyrotechnic compositions containing magnesium degrade during storage. This changes the performance of the composition and ultimately can result in the composition failing to function. It is possible to follow the ageing directly by measuring the small amount of heat released during the process using isothermal microcalorimetry. Further characterisation of the aged compositions enables a thermal property, such as ignition temperature, or the amount of a product formed to be correlated directly with the heat of ageing. However, since the sample masses used in the microcalorimeter are normally in the range 100-500 mg, there is insufficient material for the standard pyrotechnic tests including burning rate and light output measurements.

The results of ageing studies on a binary magnesium-strontium nitrate pyrotechnic composition containing equal parts by mass of the components have been reported previously [8, 9, 10] along with the pyrotechnic and thermal properties of this pyrotechnic system [11]. Isothermal microcalorimetry measurements were performed on samples at temperatures between 40 °C and 70 °C and at a range of relative humidities. Experiments were generally conducted in air using closed glass ampoules but some experiments were also undertaken in argon. Thermal analysis studies carried out on the aged samples included high temperature differential scanning calorimetry (DSC) under both ignition and non-ignition conditions. Materials from different sources were studied and the aged compositions were studied by x-ray diffraction and analysed quantitatively.

Preliminary studies on a 50% magnesium-50% strontium nitrate composition at 50 ºC and 65 % RH showed an initial induction period where a very low heat flow was observed, after 15 days the reaction rate increased rapidly and it continued at a significant rate following the peak heat flow. Repeat experiments showed that the onset time of main reaction was variable but the curves observed had similar peak sizes and shapes (Figure 1).

The heat flow from strontium nitrate was almost zero and the composition initially had a heat flow lower than that of and equivalent amount of magnesium alone (Figure 2). After 14 days the heat flow from the composition was above that of magnesium. It was concluded that the ageing

resulted from an interaction between magnesium and strontium nitrate in the presence of water vapour and a major component of the ageing process can be represented by the following equation:

$$3\ Mg + Sr(NO_3)_2 + 4\ H_2O \rightarrow 3\ Mg(OH)_2 + Sr(NO_2)_2 + H_2$$

Increasing the relative humidity from 65% to 69% RH resulted in a reduced induction period and an increase in the maximum heat flow (Figure 3). A further increase to 74% RH caused the induction period to be eliminated and a further increase in the maximum heat flow was observed.

The role of nitrite formation in rate of ageing was studied (Figure 4), the addition of 1% nitrite eliminated the induction period and a more rapid heat flow was observed after just 8.7 hrs.

Conclusions

The ammunition behaved in a way expected for materials in hazard classification 1.2 but it is recognised that a significantly larger event involving other magazines and possibly the entire complex could have occurred. The results of the pyrotechnic ageing study support the conclusions of the official investigation board [1] that ignition of the pyrotechnic composition as a cause of the accident was very unlikely. Some organisational shortcomings were also identified during the internal investigation and as a result, improvements were introduced to both the methodologies and the way they were applied. In particular, the requirement for technical expertise to be involved in the decision making process was acknowledged. Disposal of old ammunition has been accelerated and today the new system is working well.

A new surveillance system for propellants has been introduced in Finland. Additionally, an increased use of international methodologies and standards particularly the NATO Standardization Agreements (STANAGs) and Allied Ordnance Publications (AOPs) from the AC/326 Group has resulted. Where appropriate, these internationally recognized documents have been used as a foundation to support acquisition including in-service surveillance of energetic materials and munitions. Most of the AC/326-Sub-Group 1 documents have been implemented as National procedures.

Staff training across the Finnish Defence Forces and related Industry has been improved by the introduction of an Ammunition Safety Course organised by the Army Materiel Command. The course aims to increase the knowledge and competence of people working in the explosives sector, particularly the authorities, scientists and experts, in the many aspects of ammunition safety and risk assessment. The main purpose of the course has been to influence the attitude and culture of personnel in matters of safety.

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Tables

Table 1. The type and position of the ordnance.

	Distance (m)						
Type of ordnance	**50**	**100**	**200**	**250**	**300**	**350**	**>400**
Fixed ammunition	800	150					
HE projectiles	500	200	3	1			
Projectiles with fuze	650	350					
Tracered projectiles	620	200		2	5		
Tracered projectiles with fuze	3000	880	1		3		
Fuzes	100	90	1	3			1
Tracers	3200	680		27	15	12	1
Cartridge cases with primer/propellant	500	120	3				

Table 2. Historical propellant data.

	Propellant Types	Measurements	Average Number
Single based with diphenylamine	39	6183	158
Double and triple based with methyl centralite	9	421	47
Double and triple based with ethyl centralite	24	681	28

Table 3. Age groups used in cluster analysis.

Age group number	Propellant age
1	0-4 years
2	5-9 years
3	10-14 years
4	14-19 years
5	20-24 years
6	25-29 years
7	30-39 years
8	40-69 years

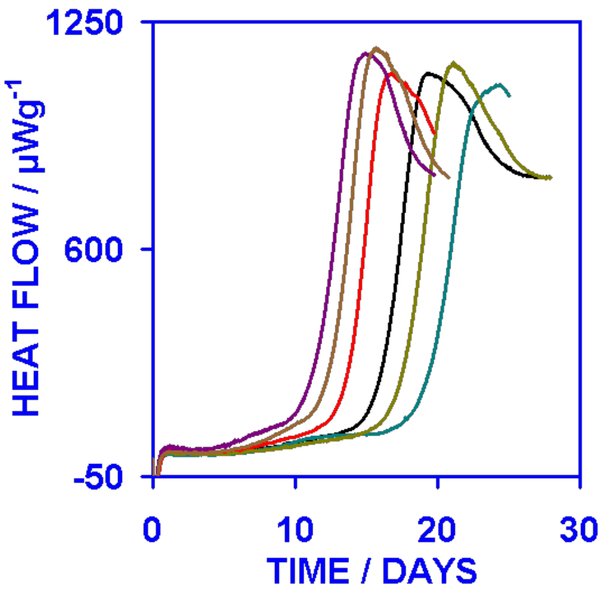

Figure 1: Heat flow for a binary mix of 50% magnesium-50% strontium nitrate at 50 ºC and 65 % RH.

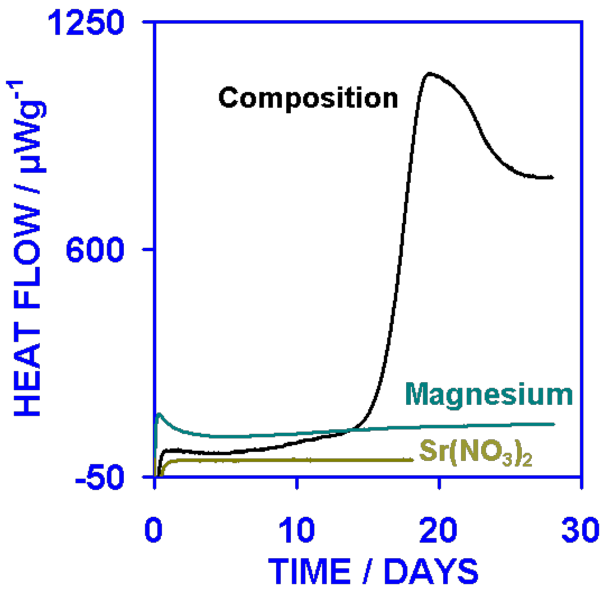

Figure 2: Comparison of heat flows for magnesium (0.5x), strontium nitrate and the binary composition at 50 ºC and 65 % RH.

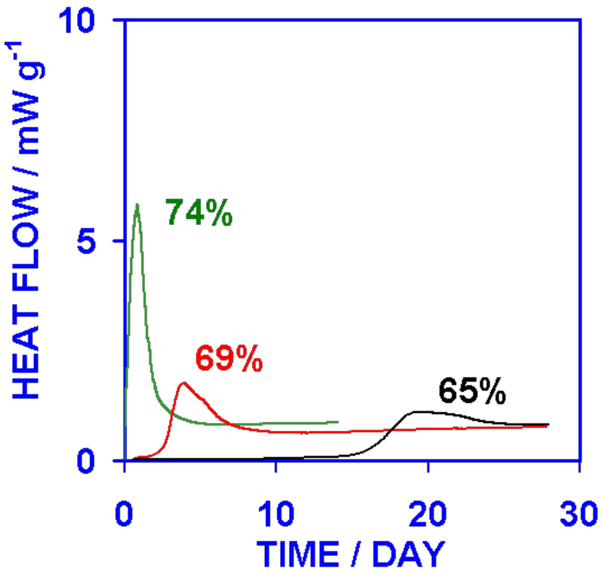

Figure 3: Heat flow for 50% magnesium-50% strontium nitrate at 50 ºC and different relative humidities.

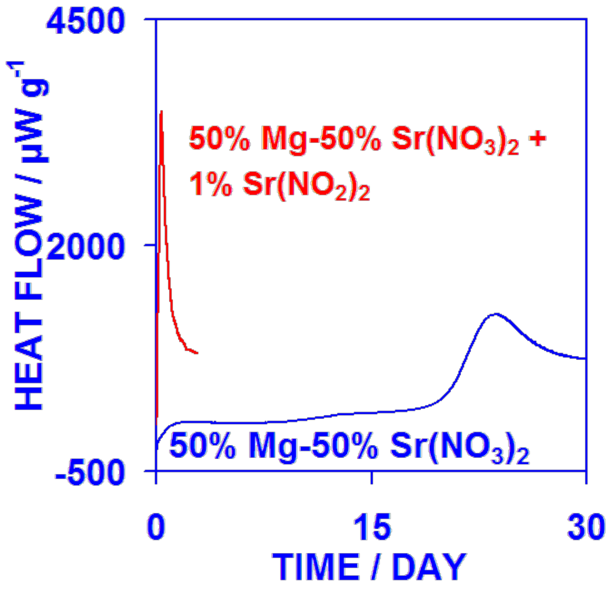

Figure 4: Heat flow curves showing the influence of adding 1% strontium nitrite.

Investigation and Site Restoration following a Major Accident Involving Hazard Classification 1.2 Ammunition

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Army Materiel Command

Army Materiel Command

- Military unit within the Army
- Headquarters in Tampere employing over 300 staff
- Four Regiments along with the Ammunition Centre and a Test Firing Centre
- Around 1700 employees in total
- The annual expenditure is one-quarter of the Finnish military budget

Scope

1. Background
2. Accident statistics
3. Propellant statistical study
4. Pyrotechnic study
5. Efforts towards NATO Standardization of Ammunition and Energetic Materials

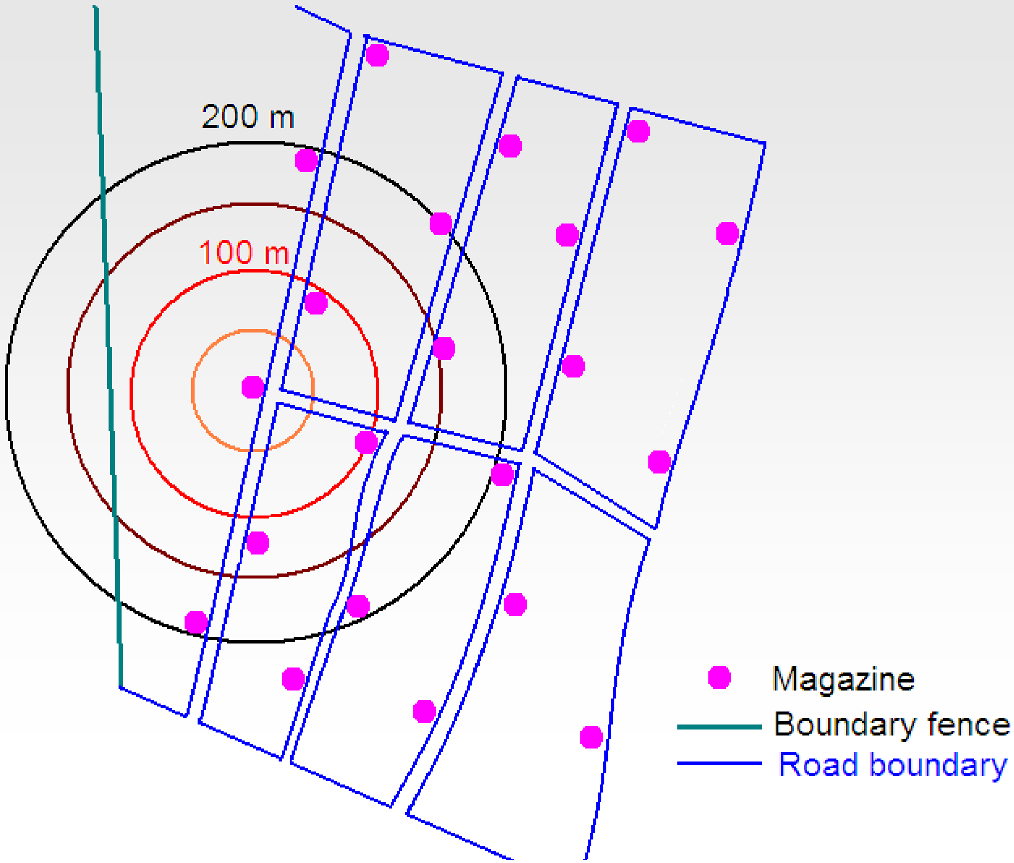
Background

- In July 1999 a storage magazine at an ammunition depot was completely destroyed by an explosion
- 1.2 ammunition (40 mm) awaiting disposal
  - High explosives
  - Fuzes
  - Double and single based propellants
  - Pyrotechnic tracers
- Unheated and unventilated magazine
  - Clad timber frame with sheet metal roof
  - Ambient temperatures up to 30 ° C
  - Magazine interior temperature up to 60 ° C

Accident statistics

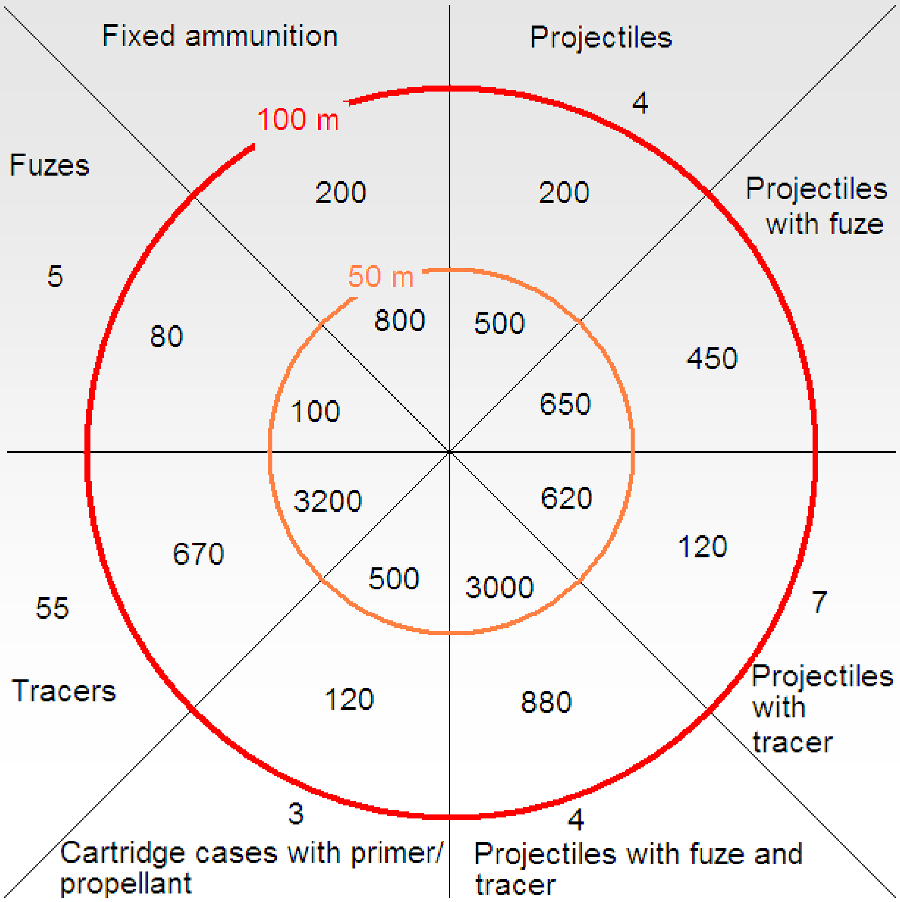
- No personnel were injured by or directly involved in the accident
- Helicopters and planes took more than 4 days to extinguish the fire
- Ordnance and energetic materials were spread over a wide area
- Debris was ejected onto the roof of a nearby magazine and through the wall of a second
  - Fire inside both buildings
    - Propellant in an ammunition container
    - Wooden pallet
  - Both self-extinguished

Accident statistics



- Fixed ammunition - 1000 items
- Projectiles - 700 items
    - fuzes and tracers - 4000 items
    - with fuzes - 1000 items
    - with tracer - 750 items
- Fuzes - 200 items
- Tracers - 4000 items
- Cartridge cases with primers and/or propellant - 600 items

Accident statistics



- Projectlies
  - One over 200 m
- Projectiles with tracer
  - Five over 250 m
- Projectiles with fuze and tracer
  - Three over 250 m
- Fuzes
  - One over 400 m
- Tracers
  - Twelve over 300 m
  - One over 400 m

Accident statistics

- The Official Accident Investigation Board concluded that

  "The most likely cause of the accident was auto-ignition of a propellant"

- Scientific investigation concluded that the degradation of the other energetic materials had not been previously studied in sufficient detail
  - Statistical study on the propellants stabiliser content
  - Degradation studies on pyrotechnics

Accident statistics

Outcomes of the accident

- An immediate plan to dispose of all propellants over 40 years old introduced
- A statistical study on propellant stabiliser content was undertaken
- The ammunition clean-up and disposal took 10 years to complete
  - Only possible during 8 months of the year
- The financial cost of the accident was extremely high

Propellant statistical study

The aims of this study were to:

- Determine if there was a relationship between age and stabiliser levels for different propellant types
- Determine if there was a relationship between the dimensions of the propellant and the stabiliser levels

Propellant statistical study

- Original lot sizes ranged from 10 000 kg to 30 000 kg
- Four magazine types
  - Light storage
  - Dry storage
  - Earth-covered buildings
  - Cave conditions
- Storage conditions for individual lots were diverse
  - Annual temperature range -50 ° C to +60 ° C
  - Annual relative humidity between 10% to 100%
- The starting stabiliser levels for most individual lots were known

Propellant statistical study

- Propellants grouped as
  - Single-based
  - Double and triple-based
- Historical data were found for >7000 stabiliser measurements
    - Around 1700 different lots
    - 72 different types
  - High Performance Liquid Chromatography
  - Ten samples for each lot of propellant were analysed
  - Up to 40 results available on a single lot of propellant

Propellant statistical study

	Propellant Types	Measurements	Average Number
Single based with diphenylamine	39	6183	158
Double and triple based with methyl centralite	9	421	47
Double and triple based with ethyl centralite	24	681	28

Propellant statistical study

Conclusions

- On average, five times as many tests were performed on single based propellants compared to the combined double and triple based propellants
- Single based propellants
  - Many had stabiliser levels < 0.5%
  - One had level of <0.1%
- Based on limited data, propellants containing ethyl centralite were generally more stable than those containing other stabilisers
- Increasing the number of samples analysed raised the probability of finding a low level of stabiliser

Propellant statistical study

Conclusions

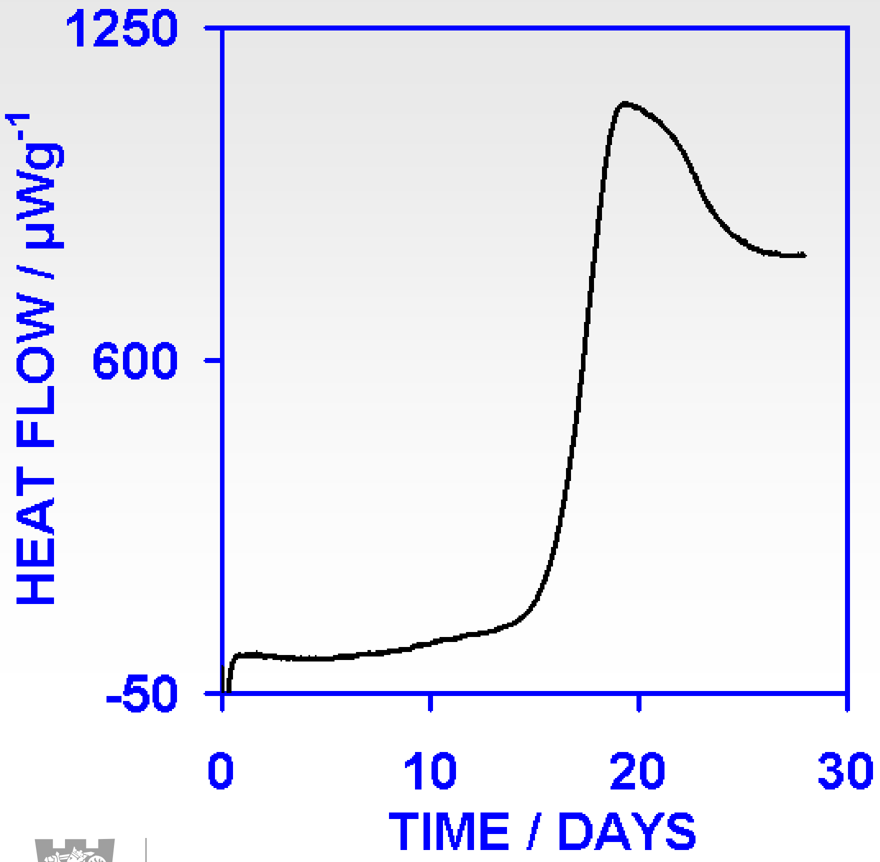
- No relationship was found between propellant grain size and stabiliser content
- The storage history and other external factors had a greater affect on the stabiliser content than propellant age
- The quality of manufacture had a significant affect on stabiliser levels

Pyrotechnic study

- Heat flow calorimeter studies
  - Range of temperatures and relative humidities
    - Closed glass ampoule
  - Range of formulations
    - Different sourced materials
  - Pressed samples
- Analysis of aged composition
  - X-ray diffraction
  - Quantitative

Pyrotechnic study

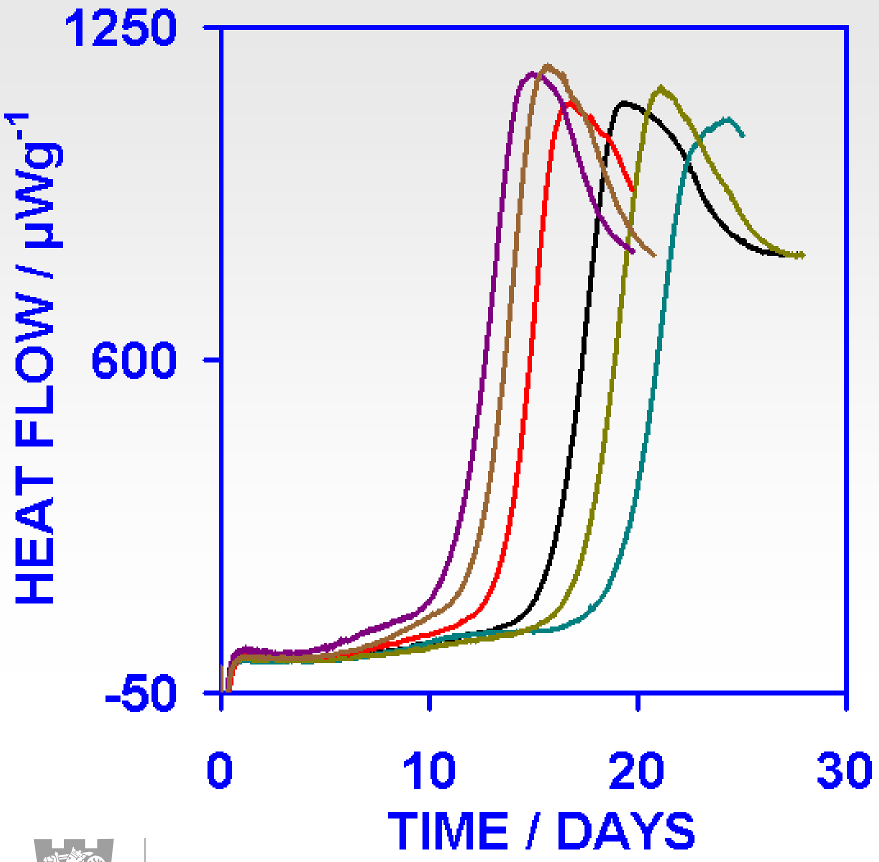
50% Mg-50% Strontium Nitrate 50 ° C and 65% RH



- Initial induction period – very low heat flow
- Reaction rate increased rapidly after 15 days
- Reaction continued at a significant rate following the peak heat flow

Pyrotechnic study

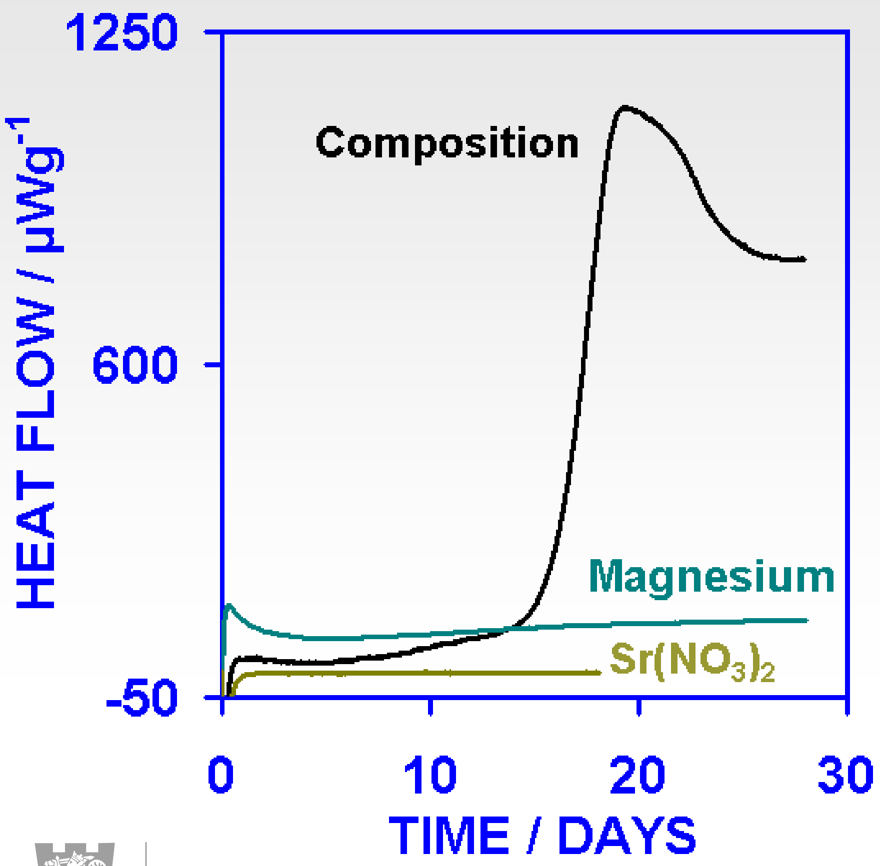
50% Mg-50% Strontium Nitrate 50 ° C and 65% RH



- Initial induction period – very low heat flow
- Reaction rate increased rapidly after 15 days
- Reaction continued at a significant rate following the peak heat flow
- Onset time of main reaction was variable
- Similar peak size and shape

Pyrotechnic study

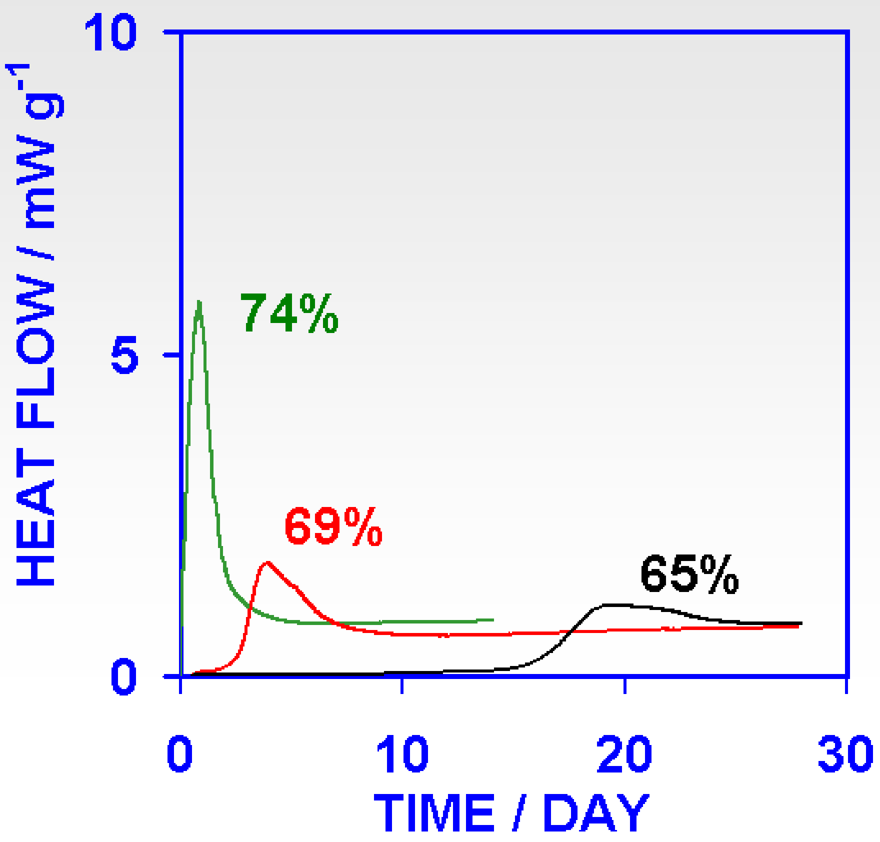
50% Mg-50% Strontium Nitrate 50 ° C and 65% RH



- Heat flow from strontium nitrate was almost zero
- Composition initially heat flow was lower than that of magnesium
- After 14 days the heat flow from the composition becomes greater
- Ageing - interaction between magnesium and strontium nitrate in the presence of water vapour

Pyrotechnic study

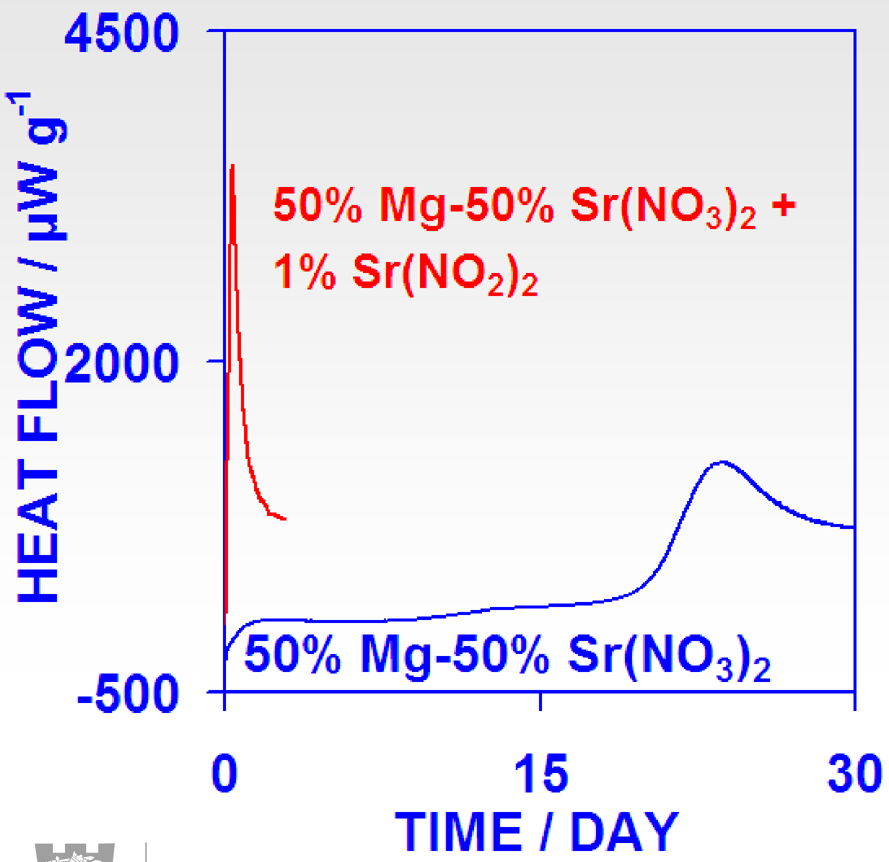
50% Mg-50% Strontium Nitrate 50 ° C



- Increasing the relative humidity from 65% to 69% RH
  - Reduced induction period
  - Increase in the maximum heat flow
- Increasing it further to 74% RH
  - The induction period was eliminated
  - Further increase in the maximum heat flow was observed

Pyrotechnic study

50% Mg-50% Strontium Nitrate 50 ° C and 65% RH



- Addition of 1% strontium nitrite
  - Eliminates the induction reaction
  - Maximum heat flow observed after 9 hrs

Pyrotechnic study

Conclusions

- At 65% RH, there was an induction period before the onset of the main degradation reaction
- A major component of the ageing process can be represented by the following equation:

$$3\ Mg + Sr(NO_3)_2 + 4\ H_2O \longrightarrow 3\ Mg(OH)_2 + Sr(NO_2)_2 + H_2$$

- The induction period was eliminated by
  - Increasing the relative humidity to 74%
  - Adding 1% strontium nitrite
- The amount of heat generated during the tracer degradation is very low

Efforts towards NATO Standardization of Ammunition and Energetic Materials

- Updating National Procedures and Instructions to bring them more into line with ”Best Practice”
- At National Level implemented some AC/326 methodologies
    - Qualification of Energetic Materials – STANAG 4170/AOP-7
    - Surveillance of Energetic Materials – STANAG 4620/AOP-48 and STANAG 4582
    - Chemical Compatibility of Ammunition Components with Explosives – STANAG 4147
- Updating and improving National practices
    - Training by Army Material Command

Efforts towards NATO Standardization of Ammunition and Energetic Materials

New System for NC Based Propellants

- Surveillance
  - STANAG 4620 & AOP-48, stabilizer content based on HPLC
  - Supporting technique given in STANAG 4582 (HFC)
- Disposal
  - Recommended by the surveillance programme

Summary

- The most likely cause of the accident was the self-ignition of the propellant
- The ammunition involved behaved in the way described in the UN Orange Book for hazard classification group 1.2
- The statistical study showed that in general age did not provide a good indication of the propellant's stabiliser content or its condition
- Ageing of the tracer composition was unlikely to generate sufficient heat to self ignite
- An important factor to maintain safety is the culture and attitude of personnel in the organisation, both those producing, and those using written instructions and methodologies
- It is important to involve the correct technical experts in the decision making processes

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